CO_2 utilization via auto-thermal catalyst-assisted chemical looping

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Carbon dioxide, a major green-house gas, has become an attractive source of carbon for the chemical industry owing to its low cost and high availability. Valorizing CO_2 towards useful chemicals is particularly interesting from both environmental and economic point of view [1]. Cyclic conversion through Catalyst-assisted Chemical looping Dry Reforming (CCDR) over a bifunctional bed composed of a physical mixture of a Ni-based reforming catalyst and a Fe-based oxygen storage material (OSM) is a novel technology for CO_2 utilization [2]. In this process, a given reaction is divided into two half-cycles: (1) CH_4 and CO_2 are first converted over Ni into H_2 and CO which reduce Fe_3O_4 to metallic Fe; (2) reduced Fe_3O_4 is regenerated via interaction with CO_2 resulting in CO production. Compared to the conventional dry reforming of CH_4, which produces syngas, CCDR is designed for maximized CO_2 conversion (three molecule of CO_2 per molecule of CH_4).

However, the overall CCDR process is strongly endothermic (ΔH_{298} = 330 kJ/mol), requiring high operating temperature and thereby leading to fast catalyst deactivation. Alternatively, the process could be rendered auto-thermal by co-feeding oxygen in close analogy to industrial auto-thermal CH_4 reforming. Here, a new process, auto-thermal catalyst-assisted chemical looping, is presented (Eq. 1).

$$CH_4 + xCO_2 + (3-x)/2O_2 \leftrightarrows (1+x)CO + 2H_2O \qquad \text{(Eq. 1)}$$

Auto-thermal catalyst-assisted chemical looping integrates two strategies [3]: CO production through Fe_3O_4/Fe chemical looping and auto-thermal catalytic conversion of CH_4, O_2 and CO_2 to syngas over the Ni-based catalyst. A small amount of O_2 is co-fed with CH_4 and CO_2 to partially convert CH_4 in an exothermic reaction (partial oxidation or combustion), generating heat in-situ and thereby compensating the strong endothermicity of the reduction reaction.

A detailed study of auto-thermal catalyst-assisted chemical looping for CO_2 utilization was carried out using different reactor bed configurations composed of core-shell structured materials, such as Ni/Zr@Zr reforming catalyst, Fe/Zr@Zr OSM and Fe/Zr@Zr@Ni@Zr bifunctional material, all of which were synthesized by a

combination of nanocoating and impregnation [4]. To optimize the efficiency of this process, the distribution of reforming catalyst and OSM was assessed based on the concept of double or single-mixed layer bed as well as the on a bifunctional material bed (Figure 1a), all of which were expected to work in different modes (Figure 1b).

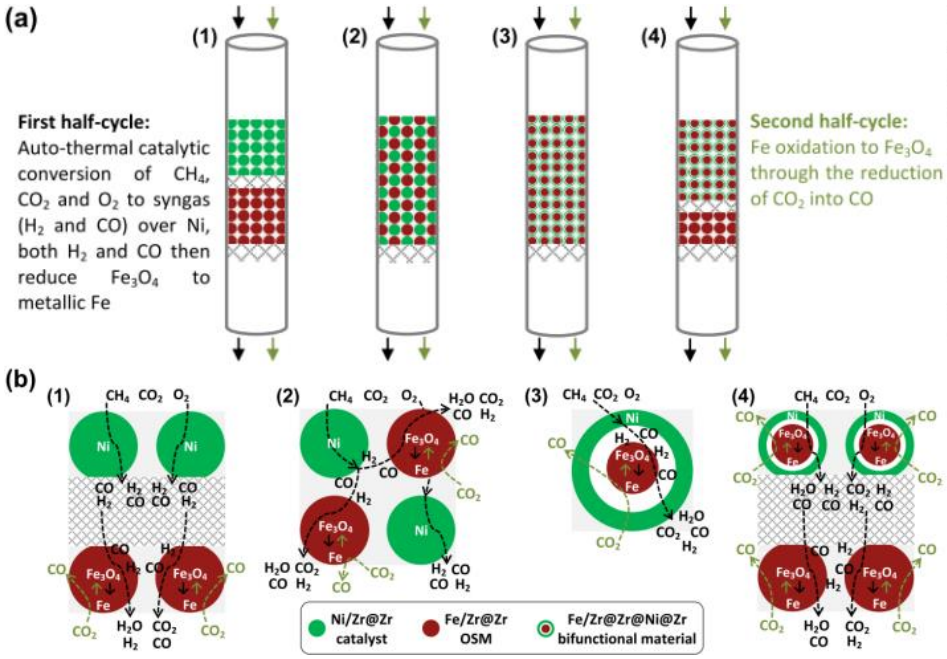

Figure 1. (a) Schematic representation of the auto-thermal catalyst-assisted chemical looping process for CO_2 utilization over different reactor bed configurations composed of core-shell structured materials and the corresponding work modes **(b)** during the whole process.

In-situ XRD characterization allowed to monitor the evolution of crystallographic phases of the materials during redox cycling. The morphological changes of materials were examined by STEM-EDX after 25 cycles. The double-mixed layer of Fe/Zr@Zr@Ni@Zr and Fe/Zr@Zr (Figure 1a-b4) exhibits highest CH_4 and CO_2 conversion to CO at the 750 ~ 900 °C, making it the most suitable configuration for the auto-thermal catalyst-assisted chemical looping process.

References

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